

UNITED STATES PATENT OFFICE

2,168,691

GASOLINE REFINING

Vanderveer Voorhees, Hammond, Ind., assignor
to Standard Oil Company, Chicago, Ill., a cor-
poration of Indiana

Application September 8, 1936, Serial No. 99,705

5 Claims. (Cl. 196—13)

This invention relates to the manufacture of motor fuels and more especially to motor fuels of the character of gasoline, having a high knock rating. One of the objects of the invention is to separate ordinary motor fuel into constituents of high knock rating and low knock rating to provide a high knock rating fuel for high compression internal combustion engines. The low knock rating fraction may be employed in low compression engines or for special purposes such as in the manufacture of solvent naphthas, stove gasoline and the like.

A particular object of the invention is to provide high knock rating aviation gasoline by separating straight run aviation gasoline into fractions containing on the one hand straight chain or normal paraffinic hydrocarbons and on the other hand naphthenic and branched chain paraffinic hydrocarbons. For convenience these two classes of hydrocarbons will be termed herein "detonating" and "non-detonating" hydrocarbons respectively.

It is well-known that gasoline is composed of hydrocarbons representing a wide variety of chemical classes such as the aromatic hydrocarbons, the naphthenes, the normal paraffines, branched paraffines and substituted naphthenes and aromatics. Of these different classes of hydrocarbons it has been shown that the normal paraffines are especially susceptible to detonation when employed as a fuel in a high compression internal combustion engine. By high compression engines is meant engines having compression ratios above 5:1. The recent trend in automobile engine design has resulted in a general raising of the compression ratio, even as high as 6.5:1, with marked fuel economies and reduction in engine weight per horsepower unit. This trend has been even more pronounced in the design of aviation engines where increased fuel economy and reduced engine weight is still more important.

In order to supply these high compression engines with a suitable fuel, petroleum refiners have been required to resort to the use of anti-detonants, particularly lead tetraethyl. However, this is expensive and, furthermore, the amount which can be used with profit is quite limited. In aviation fuel, for example, the maximum allowable in many specifications is 3 ml. per gal. Larger amounts are considered undesirable from the standpoint of erosion, deposits on valves, etc. Furthermore, the relative effectiveness of the anti-detonant decreases rapidly as the amount employed increases.

In order to make the high knock rating aviation fuels with knock ratings above 80 or 85 octane number, refiners have been required to resort to special methods of separation of specific types of hydrocarbons or even to the synthesis of specific hydrocarbons such as so-called iso-octane (2-2-4-trimethyl pentane). Aromatic and olefinic hydrocarbons which are suitable for medium compression engines operating at low temperatures are ineffective in aviation work where the compression ratios are unusually high and a high temperature effect causes much of the anti-knock property of these fuels to disappear.

Numerous processes have been described for separating the olefin hydrocarbons from the paraffin hydrocarbons to improve the knock rating of fuels for moderately high compression service. Extraction with selective solvents, liquid sulfur dioxide, etc. has been employed and these processes may be used quite successfully because of the chemical affinity between olefines and various selective solvents. The separation of the naphthenes and branched paraffines from straight-run gasoline, however, is a much more difficult problem and many attempts to solve it have been made. One such method is the extreme fractionation of the fuel in an attempt to separate it into individual hydrocarbons which may then be combined in accordance with their knocking characteristics. This method requires extremely high reflux ratios in fractionation thereby augmenting the cost of the operation to an inordinate degree.

Another method which has been proposed for separating closely boiling hydrocarbons of slightly differing chemical character is fractionation in the presence of a selective solvent which has the property of depressing the vapor pressure of one of the hydrocarbon constituents. I am aware of U. S. Patent 1,948,777 by C. O. Young and G. A. Perkins describing such a process for the separation of closely boiling diolefines and paraffin hydrocarbons. I am also aware of British Patent No. 324,350 to J. Y. Johnson for separating mixtures of closely boiling hydrocarbons such as butadiene and butylene by this method. The process described by these patents, however, is incapable of separating widely boiling mixtures of hydrocarbons such as gasoline, containing a vastly greater number of individual hydrocarbons.

In accordance with the present invention gasoline is separated into its detonating and non-detonating constituents by a unique combination of fractional distillation in the presence of selec-

tive high boiling solvents and an extremely efficient process of fractionation without solvents. The invention will be more readily understood by referring to the accompanying drawing which forms a part of this specification.

Referring to the drawing, I represents a fractionating column of an especially efficient type suitably packed with bubble caps and plates. It is desirable that column I should contain at least 15 plates and 25 plates or more are desirable. Column II is provided for fractionating the vapors derived from column I in contact with the selective high boiling solvent and it is preferred to have the column II packed with a contacting material such as rings, springs, etc. which provide maximum contacting surface with minimum liquid hold-up.

In carrying out the process, gasoline, which may be a straight-run Mid-Continent gasoline boiling up to 400° F. or an aviation gasoline boiling up to 280° F. for example, may be charged by line 10 to batch still 11. Heat applied to the still by steam coil or by burner 12 causes the gasoline to distil through fractionating column I provided with dephlegmator 13. Cooling water or other refrigerant is supplied to the dephlegmator by line 14 and refluxed condensate is led by line 15 regulated by valve 16 to the upper part of the column I. The reflux ratio may be varied considerably, depending upon the speed of distillation, the number of plates and efficiency of the fractionating column I, but a reflux ratio of 5:1 may suitably be employed.

The vapors from column I are led by line 17 to column II where they are contacted with a down-flowing stream of selective solvent and reflux condensate. The solvent is admitted to column II by line 18 and intimately contacts the upflowing vapors, selectively associating with the non-detonating type hydrocarbons and carrying them downward to the base of the column II where they may be partially revaporized by means of re-boiling coil 19.

The uncondensed vapors from column II pass by line 20 to dephlegmator 21 where a portion is condensed and returned by reflux line 22 and valve 23. Vapors remaining uncondensed are led by line 24 to condenser 25 and thence to receiver 26 from which the low knock rating fraction of the gasoline is withdrawn by line 27.

The solvent and reflux condensate is withdrawn from column II by line 28 leading to fractionating column 29 equipped with reboiling coil 30 and reflux coil 31. The gasoline is vaporized from the solvent in this column and is led by vapor line 32 to condenser 33 and thence to receiver 34 where it forms a high knock rating fraction of the gasoline and may be withdrawn by line 35.

The solvent collecting in the bottom of column 29, now substantially stripped of its gasoline component, is conducted by line 36 to pump 37 whence it flows back to the upper part of column II by line 18. Cooler 38 may be employed to reduce the temperature to that of the column II at the point of entry of line 18. Make-up solvent may be introduced to the system by valved line 39 when necessary.

In the operation of my process it is essential to produce by column I a vapor which, if condensed, would have a narrow boiling range, preferably within about 5° F. at any one particular time although under certain conditions a distillate having a boiling range of about 10° F. may be employed successfully. The feature of my process which especially characterizes it is the

production of a continuous series of very narrow boiling gasoline fractions from a wide boiling gasoline and the simultaneous separation of the narrow boiling fractions by further fractionation in the presence of a selective solvent. In this way I am enabled to effect the desired separation of the gasoline into "paraffinic" and "naphthenic" constituents by a process which would be totally inapplicable to the original wide boiling gasoline as it must be understood that the separation of such closely related hydrocarbons, saturated naphthenes and paraffines by the solvent distillation method can only be effected with extremely close boiling components since the chemical association between the selective solvent and the naphthenes is only capable of depressing the boiling point of these compounds by a few degrees.

Various selective solvents may be used in my process for refluxing in column II, but it is essential that they be "polar" type liquids and that they possess boiling points above the boiling range of the hydrocarbon fraction being treated, so that they may be readily separated from the gasoline. As examples of such solvents I may mention the following organic solvents glycol, nitrobenzene, glycerin, ethylene chlorhydrin, glacial acetic acids, furfural, beta beta' dichlor diethyl ether, aniline, cresylic acid, phenol, mono chlorphenol, dichlor phenol, esters of phthalic acid as methyl, ethyl and butyl phthalate, chlor acetate and tri-chlor acetate, etc.

As an example of the application of this invention to separation of a typical gasoline, the process may be applied to a midcontinent aviation gasoline having the following boiling range:

	Degrees F.
Initial -----	117
10% -----	152
50% -----	178
90% -----	211
End point -----	258

The knock rating of this gasoline may be 62 octane number and after separating into detonating and non-detonating fractions by the present process the non-detonating fraction may have a knock rating of 80 octane number, that is, be equivalent to a mixture of 80% of iso-octane in normal heptane.

In a modification of my invention I may segregate the fractions obtained from fractionation with solvent in column II according to their knock rating, especially the fractions removed with the solvent at the base of the column. Although the detonating hydrocarbons escape at the top of the column II and the non-detonating hydrocarbons at the bottom, these streams each vary in antiknock effect from time to time as the distillation progresses, and it is a part of my invention to combine the higher knock rating fractions and the lower knock rating fractions separately to produce two or more grades of anti-knock gasoline.

I claim:

1. The process of separating gasoline containing a complex mixture of paraffinic and naphthenic hydrocarbons of wide range in boiling points, into a detonating paraffinic and a non-detonating naphthenic fraction which comprises initially distilling said gasoline through an efficient fractionating zone, removing from said fractionating zone gasoline vapors comprised of hydrocarbons having, at a given time interval, substantially the same boiling points but different chemical characteristics, continuously and imme-

diately introducing said hydrocarbon vapors, without condensation into a second fractionating zone, therein contacting the said vapors with a selective high boiling organic polar liquid and removing from said second fractionating zone gasoline vapors composed substantially of detonating paraffinic hydrocarbons, and reflux condensate composed substantially of non-detonating naphthenic hydrocarbons associated with said polar liquid, and separating the said non-detonating hydrocarbons from said liquid.

2. The process of claim 1 wherein the polar liquid which is separated from the said non-detonating hydrocarbons is recycled to the said second fractionating zone.

3. The process of separating the naphthenic constituents from the paraffinic constituents of a complex mixture of petroleum hydrocarbons having a relatively wide boiling range, which comprises heating a body of said hydrocarbon mixture in a confined space, withdrawing a stream of vapor from said body of hydrocarbons, subjecting said vapor stream to a high degree of fractionation in a first fractionating stage, thereby producing a continuous stream of vapors of naphthenic and paraffinic hydrocarbons of substantially uniform molecular weight at any given time but increasing as the vaporization of said body progresses, immediately and without condensation subjecting said stream of hydrocarbons of uniform but progressively increasing molecular weight to further fractionation in a second stage in the presence of an organic polar liquid of relatively high boiling point whereby the said naphthenic hydrocarbons are associated with said polar liquid, withdrawing vapors of said paraffinic hydrocarbons from said second stage of

fractionation, withdrawing said polar liquid and associated naphthenic hydrocarbons from said second stage of fractionation and recovering said naphthenic hydrocarbons therefrom.

4. The process of separating the naphthenic constituents from the paraffinic constituents of a complex mixture of petroleum hydrocarbons having a relatively wide boiling range, which comprises heating a body of said hydrocarbon mixture in a confined space, withdrawing a stream of vapor from said body of hydrocarbons, subjecting said vapor stream to a high degree of fractionation in a first fractionating stage, thereby producing a continuous stream of naphthenic and paraffinic hydrocarbons of substantially uniform molecular weight at any given time but increasing as the vaporization of said body progresses, immediately and without accumulation subjecting said stream of hydrocarbons of uniform but progressively increasing molecular weight to further fractionation in a second stage in the presence of an organic polar liquid of relatively high boiling point whereby the said naphthenic hydrocarbons are associated with said polar liquid, withdrawing vapors of said paraffinic hydrocarbons from said second stage of fractionation, withdrawing said polar liquid and associated naphthenic hydrocarbons from said second stage of fractionation and recovering said naphthenic hydrocarbons therefrom.

5. The process of claim 4 wherein an instantaneous sample selected from the said continuous stream of naphthenic and paraffinic hydrocarbons of substantially uniform molecular weight introduced into said second fractionation stage is characterized by a boiling range within 10° F.

VANDERVEER VOORHEES.